Atomic and molecular alignment from photoelectron angular distributions in $(n+1)$ resonantly enhanced multiphoton ionization

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Two distinct $(n+1)$ REMPI techniques for obtaining the alignment of gas phase atoms and molecules from photoelectron angular distributions are presented. In both methods, the alignment is extracted from the angular distributions *independently* of the photoionization dynamics. The first method, which takes advantage of circular dichroism in the angular distributions (CDAD) has already been established experimentally as a useful probe of state alignment. The theory outlined in previous work is expanded here. The second method involves photoionization with light *linearly polarized along the photoelectron collection direction* and is presented here for the first time.

I. INTRODUCTION

The investigation of gas phase atomic and molecular alignment has been intense in recent years. Alignment of atoms and molecules occurs by a variety of processes including particle excitation,[1] surface scattering,[2] photoabsorption,[3–5] photodissociation,[6–15] interaction with external fields,[16–18] etc. Conventionally, fluorescence techniques are used to prove this state alignment. When the state of interest does not fluoresce itself,[6,7,14,19] laser induced fluorescence (LIF) methods are used. Both one-[8,9,15,20–22] and two-photon[10–13,23] LIF schemes are now common. Saturated laser optical pumping has been coupled to LIF to probe state alignment as well.[24] On the other hand, angle-resolved $(n+1)$ resonantly enhanced multiphoton ionization (REMPI) is not commonly used to probe state alignment. The bound–free nature of the ionization step, coupled with the anisotropy associated with photon absorption, causes the state alignment information to be intimately entangled with the photoionization dynamics. Even angle-integrated cross sections from $(n+1)$ REMPI contain alignment information mixed with the photoionization dynamics.[25]

In this paper we present two distinct methods for probing initial state alignment using photoelectron angular distributions obtained from $(n+1)$ REMPI processes. Both these methods determine the initial state alignment *independently* of the photoionization dynamics. The first method takes advantage of circular dichroism in the angular distributions (CDAD).[26–30] $(n+1)$ CDAD has already been established experimentally as a useful technique for the study of state alignment.[31,32] Here we present many important features of CDAD which have been presented previously only in condensed form.[29,30] The second method, introduced here for the first time, involves $(n+1)$ REMPI with the ionization laser linearly polarized along the photoelectron collection direction. For convenience, we will refer to this angle-resolved $(n+1)$ REMPI technique as PINDAD: *p*olarization *in*to *d*etector-*a*ngular *d*istributions.

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II. THEORY

We treat both $(n+1)$ REMPI methods as two steps[28,33]: (1) n-photon excitation to a resonant intermediate state, and (2) one-photon ionization of the intermediate state.

A. n-photon excitation to the intermediate state

In both CDAD and PINDAD experiments the first step is n-photon excitation of the initial state to a resonant intermediate state by light linearly polarized along the laboratory frame z axis. The intermediate state alignment will depend on the initial state alignment and the anisotropy of the n-photon absorption process.

Consider one-photon absorption from an initial state with total angular momentum J'' and relative substrate populations $N_{M_{J''}}$. The relative excited state populations, $N_{M_{J'}}$, following one-photon absorption of light linearly polarized along the laboratory frame z axis, are given by

$$N_{M_{J'}} = \sum_{M_{J''}} N_{M_{J''}} \begin{pmatrix} J' & 1 & J'' \\ M_{J'} & 0 & -M_{J''} \end{pmatrix}^2 \langle J' \| D \| J'' \rangle^2, \tag{1}$$

where $\langle J' \| D \| J'' \rangle$ is a reduced matrix element whose value will be set equal to unity for now. The $N_{M_{J''}}$ are normalized such that[29]

$$\sum_{M_{J''}} N_{M_{J''}} = 1. \tag{2}$$

As discussed in Ref. 29, an attractive alternative to the N_{M_J} description of alignment is the A_L description, where the A_L's are the state multipole moments[21]:

$$N_{M_J} = \sum_L A_L \, T_L^{M_J}. \tag{3}$$

Here,

$$T_L^{M_J} = (-1)^{J-M_J} (2L+1)^{1/2} \begin{pmatrix} J & J & L \\ M_J & -M_J & 0 \end{pmatrix}. \tag{4}$$

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TABLE I. Analytical expressions for C_{00}, C_{02}, and C_{22} for one-photon absorption.

Branch	C_{00}	C_{02}	C_{22}
P	$\frac{1}{3[(2J''+1)(2J''-1)]^{1/2}}$	$\frac{-1}{3(2J''+1)}\left[\frac{(2J''-3)(J''-1)}{5J''(2J''-1)}\right]^{1/2}$	$\frac{5[(J''-1)(J''+1)(2J''+3)(2J''-3)]^{1/2}}{21J''(2J''+1)(2J''-1)}$
Q	$\frac{1}{3(2J''+1)}$	$\frac{1}{3(2J''+1)}\left[\frac{(2J''-1)(2J''+3)}{5J''(J''+1)}\right]^{1/2}$	$\frac{(11J''^2+11J''-15)}{21J''(J''+1)(2J''+1)}$
R	$\frac{1}{3[(2J''+1)(2J''+3)]^{1/2}}$	$\frac{-1}{3(2J''+1)}\left[\frac{(2J''+5)(J''+2)}{5(J''+1)(2J''+3)}\right]^{1/2}$	$\frac{5[(J''+2)(J'')(2J''+5)(2J''-1)]^{1/2}}{21(J''+1)(2J''+1)(2J''+3)}$

Substituting Eqs. (3) and (4) into Eq. (1) and rearranging we get

$$A_{\mathbf{L}}=\sum_{L'}\tilde{A}_{L'}\cdot C_{L'\mathbf{L}}. \tag{5}$$

For a given set of initial state alignment parameters $\tilde{A}_{L'}$ (here the tilde indicates the initial state), Eq. (5) can be used to calculate the intermediate state alignment parameters $A_{\mathbf{L}}$ after n-photon absorption. For one-photon absorption, the $C_{L'\mathbf{L}}$ are given by

$$C_{L'\mathbf{L}}=(-1)^{\mathbf{L}+1}[(2L''+1)(2\mathbf{L}+1)]^{1/2}\times\sum_{\mathbf{L}}(2\mathbf{L}+1)\begin{Bmatrix}1 & 1 & \mathbf{L}\\ J' & J' & \mathbf{L}\\ J'' & J'' & L''\end{Bmatrix}\times\begin{pmatrix}1 & 1 & \mathbf{L}\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}L'' & \mathbf{L} & \mathbf{L}\\ 0 & 0 & 0\end{pmatrix}. \tag{6}$$

For the case of two-photon absorption the $C_{L'\mathbf{L}}$ are given by[10] (see Ref. 34 for an exception)

$$C_{L'\mathbf{L}}=(-1)^{\mathbf{L}}[(2L''+1)(2\mathbf{L}+1)]^{1/2}\times\sum_{\mathbf{L}}(2\mathbf{L}+1)\begin{Bmatrix}2 & 2 & \mathbf{L}\\ J' & J' & \mathbf{L}\\ J'' & J'' & L''\end{Bmatrix}\times\begin{pmatrix}2 & 2 & \mathbf{L}\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}L'' & \mathbf{L} & \mathbf{L}\\ 0 & 0 & 0\end{pmatrix}. \tag{7}$$

We restrict our consideration to initial states which are "aligned" (substrates of the same $|M_{J'}|$ have the same population) and not "oriented" (no restriction on relative $M_{J'}$ population). In this case, both L'' and $\mathbf{L}$ are even.[21,22] Simplified analytical expressions for C_{00}, C_{02}, and C_{22} for both one- and two-photon absorption are given in Tables I and II.

The relationship between the state multipole moments $\tilde{A}_0$ and $\tilde{A}_2$ and the alignment parameters $A_0^{(2)}$ commonly extracted from LIF experiments is given by[10]

$$A_0^{(2)}=\left[\frac{(2J''+3)(2J''-1)}{5J''(J''+1)}\right]^{1/2}\cdot\frac{\tilde{A}_2}{\tilde{A}_0}. \tag{8}$$

B. Photoionization of the resonant intermediate state

In Ref. 28, the differential cross section for photoionization of a resonant intermediate state was written in the form

$$\frac{\partial\sigma}{\partial\Omega_{\hat{k}}\partial\Omega_{\hat{p}}}=\sum_{\substack{L,L',M'\\ M_{J'}}}N_{M_{J'}}\beta_{LL'M'}^{M_{J'}\mu_0}Y_{L-M'}(\theta_k,\phi_k)Y_{L'M'}(\theta_p,\phi_p), \tag{9}$$

where

$$\beta_{LL'M'}^{M_{J'}\mu_0}=(-1)^{\mu_0}(2L'+1)^{1/2}\begin{pmatrix}1 & 1 & L'\\ -\mu_0 & \mu_0 & 0\end{pmatrix}\beta_{LL'M'}^{M_{J'}}. \tag{10}$$

In Eq. (9), (θ_k,ϕ_k) denotes the collection angle of the photoelectron and (θ_p,ϕ_p) denotes the photon polarization direction for linearly polarized light or the photon propagation direction for circularly polarized light. All the angles are measured in the laboratory frame. $N_{M_{J'}}$ represents the relative populations of the $M_{J'}$ sublevels for the state being ionized and $\beta_{LL'M'}^{M_{J'}\mu_0}$ contains all the dynamical information

TABLE II. Analytical expressions for C_{00}, C_{02}, and C_{22} for two-photon absorption.

Branch	C_{00}	C_{02}	C_{22}
O	$\frac{1}{5[(2J''+1)(2J''-3)]^{1/2}}$	$\frac{-2}{7}\left[\frac{(J''-2)(2J''-5)}{5(J''-1)(2J''+1)(2J''-1)(2J''-3)}\right]^{1/2}$	$\frac{1}{7(2J''-1)}\left[\frac{(2J''+3)(J''-2)(2J''-5)(J''+1)}{J''(J''-1)(2J''-3)(2J''+1)}\right]^{1/2}$
P	$\frac{1}{5[(2J''+1)(2J''-1)]^{1/2}}$	$\frac{(J''+5)}{7(2J''+1)}\left[\frac{(2J''-3)}{5J''(J''-1)(2J''-1)}\right]^{1/2}$	$\frac{(J''^2-7)}{7J''(2J''-1)(2J''+1)}\left[\frac{(2J''+3)(2J''-3)}{(J''-1)(J''+1)}\right]^{1/2}$
Q	$\frac{1}{5(2J''+1)}$	$\frac{(2J''+5)(2J''-3)}{7(2J''+1)[5J''(J''+1)(2J''-1)(2J''+3)]^{1/2}}$	$\frac{3[J''(J''+1)(2J''+5)(2J''-3)+21]}{7J''(J''+1)(2J''-1)(2J''+1)(2J''+3)}$
R	$\frac{1}{5[(2J''+1)(2J''+3)]^{1/2}}$	$\frac{(J''-4)}{7(2J''+1)}\left[\frac{(2J''+5)}{5(J''+1)(J''+2)(2J''+3)}\right]^{1/2}$	$\frac{[(J''+1)^2-7]}{7(J''+1)(2J''+1)(2J''+3)}\left[\frac{(2J''+5)(2J''-1)}{J''(J''+2)}\right]^{1/2}$
S	$\frac{1}{5[(2J''+1)(2J''+5)]^{1/2}}$	$\frac{-2}{7}\left[\frac{(J''+3)(2J''+7)}{5(J''+2)(2J''+1)(2J''+3)(2J''+5)}\right]^{1/2}$	$\frac{1}{7(2J''+3)}\left[\frac{(2J''+7)(J'')(2J''-1)(J''+3)}{(J''+2)(J''+1)(2J''+1)(2J''+5)}\right]^{1/2}$

about the photoionization process. Also $\mu_0 = 0$ for linearly polarized light, $\mu_0 = +1$ or -1 for left or right circularly polarized light, respectively, and $Y_{LM}(\theta,\phi)$ is a spherical harmonic. Although Eqs. (9) and (10) are appropriate for photoionization of both atomic and molecular states,[28] only the molecular case will be considered here.

In Ref. 28, an expression for $\beta_{LL'M'}^{M_J,\mu_0}$ is given which explicitly contains quantum numbers for the total (J_+) and rotational (N_+) angular momentum of the ion, as well as the projection of these quantities and the photoelectron and ion spin on the laboratory z axis. This expression is very cumbersome, and for the experiments of interest here, these quantities remain unresolved.[31,32] In this case, these quantum numbers can be summed over, and a much simpler expression for $\beta_{LL'M'}^{M_J,\mu_0}$ obtained. The equivalence of the rotationally explicit form[28] and the simple form is well known[35–38]; the derivation is very tedious and will not be given here.[39] Recently, Hansen and Berry derived this simpler form for the specific case of $(l+1)$ REMPI from an unaligned initial state.[38]

The simplified expression for $\beta_{LL'M'}^{M_J,\mu_0}$ for photoionization of a state described in Hund's case (b)[40] is

$$\beta_{LL'M'}^{M_J,\mu_0} = \frac{4\pi}{3} K \sum_{\substack{l\lambda\mu \\ l'\lambda'\mu' \\ \mathscr{L}}} \bar{r}_{fi}^{(\mu)} \bar{r}_{fi}^{(\mu')*} e^{i(\eta_l - \eta_{l'})} (-i)^l (i)^{l'} (-1)^P$$
$$\times (2N'+1)(2J'+1)(2\mathscr{L}+1)[(2l+1)(2l'+1)(2L+1)(2L'+1)]^{1/2}$$
$$\times (-1)^{S'+2J'-M_{J'}+\Lambda'} \begin{Bmatrix} J' & N' & S' \\ N' & J' & \mathscr{L} \end{Bmatrix} \begin{pmatrix} J' & J' & \mathscr{L} \\ M_{J'} & -M_{J'} & 0 \end{pmatrix} \begin{pmatrix} N' & N' & \mathscr{L} \\ \Lambda' & -\Lambda' & 0 \end{pmatrix}$$
$$\times \begin{pmatrix} L & L' & \mathscr{L} \\ -M' & M' & 0 \end{pmatrix} \begin{pmatrix} L & L' & \mathscr{L} \\ \lambda'-\lambda & \mu-\mu' & 0 \end{pmatrix} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & L \\ \lambda & -\lambda & \lambda'-\lambda \end{pmatrix}$$
$$\times \begin{pmatrix} 1 & 1 & L' \\ \mu_0 & -\mu_0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & L' \\ \mu' & -\mu & \mu-\mu' \end{pmatrix}, \tag{11}$$

where

$$P = \mu_0 + L + L' + \lambda' + \mu. \tag{12}$$

In the single-particle picture, $\bar{r}_{fi}^{(\mu)}$ is the dipole matrix element between the initial orbital and the photoelectron wave function in the molecular frame; its form is given in Ref. 41. K is a proportionality constant which depends on the photon energy.[42] Excluding spin (i.e., $S' = 0$) Eq. (11) is identical to that obtained by averaging the expression for a perfectly oriented[43] molecule over a distribution of orientations $|Y_{J'M_{J'}}|^2$.[35–38]

Converting the $N_{M_{J'}}$ description of alignment to the A_L description by substituting Eqs. (3), (4), and (10)–(12) into Eq. (9), summing over $M_{J'}$, and observing the orthogonality of the $3j$ symbols[44]:

$$\sum_{M_{J'}} \begin{pmatrix} J' & J' & \mathbf{L} \\ M_{J'} & -M_{J'} & 0 \end{pmatrix} \begin{pmatrix} J' & J' & \mathscr{L} \\ M_{J'} & -M_{J'} & 0 \end{pmatrix} = (2\mathbf{L}+1)^{-1} \delta_{\mathbf{L},\mathscr{L}} \tag{13}$$

we obtain

$$\frac{\partial\sigma}{\partial\Omega_{\hat{k}}\partial\Omega_{\hat{p}}} = \sum_{\substack{L,L',M' \\ \mathbf{L}}} A_{\mathbf{L}} \beta_{LL'M'}^{\mathbf{L}\mu_0} Y_{L-M'}(\theta_k,\phi_k) Y_{L'M'}(\theta_p,\phi_p) \tag{14}$$

with

$$\beta_{LL'M'}^{\mathbf{L}\mu_0} = \sum_{M_{J'}} T_{\mathbf{L}}^{M_{J'}} \beta_{LL'M'}^{M_J,\mu_0} \tag{15a}$$
$$= \frac{4\pi}{3} K \sum_{\substack{l\lambda\mu \\ l'\lambda'\mu'}} r_{fi}^{-(\mu)} r_{fi}^{-(\mu')*} e^{i(\eta_l - \eta_{l'})} (-i)^l (i)^{l'} (-1)^P$$
$$\times (2N'+1)(2J'+1)[(2\mathbf{L}+1)(2l+1)(2l'+1)(2L+1)(2L'+1)]^{1/2}$$
$$\times (-1)^{S'+J'+\Lambda'} \begin{Bmatrix} J' & N' & S' \\ N' & J' & \mathbf{L} \end{Bmatrix} \begin{pmatrix} N' & N' & \mathbf{L} \\ \Lambda' & -\Lambda' & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & L' \\ \mu' & -\mu & \mu-\mu' \end{pmatrix}$$
$$\times \begin{pmatrix} L & L' & \mathbf{L} \\ -M' & M' & 0 \end{pmatrix} \begin{pmatrix} L & L' & \mathbf{L} \\ \lambda'-\lambda & \mu-\mu' & 0 \end{pmatrix} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & L \\ \lambda & -\lambda' & \lambda'-\lambda \end{pmatrix} \begin{pmatrix} 1 & 1 & L' \\ \mu_0 & -\mu_0 & 0 \end{pmatrix}. \tag{15b}$$

Equation (14) is very general. The alignment information for the state being ionized is contained solely in the moments A_L. Nothing has been said about how the alignment is attained, whether it be by photoabsorption, photofragmentation, collisions, external fields, etc.

The most important result contained in Eq. (14) is that the index L of the alignment *is different* from that of the photoelectron, L. For photoelectron angular distributions in general, then, the alignment information is intimately intertwined with the photoionization dynamics. Even angle-integrated cross sections, in which an integration over (θ_k,ϕ_k) forces $L = 0$, are dependent on alignment.[25] Until recently, this complexity has discouraged the use of photoelectron angular distributions for extraction of alignment information. However, as we now demonstrate, two distinct experiments are possible which both yield the alignment information in a straightforward manner, independently of the photoionization dynamics.

III. EXPERIMENT 1: CDAD

The usefulness of CDAD as a probe of gas phase molecular alignment has now been established both theoretically and experimentally.[28–32] Nevertheless, many of the important properties of the CDAD spectra have been given previously in condensed form,[29,30] without the detailed analysis presented here.

A. A simple picture for understanding CDAD

Traditionally, one thinks of circular dichroism or optical activity in terms of mirror images and symmetry planes or the lack thereof.[45] Circular dichroism is normally associated with chiral molecules and not with gas phase aligned atoms and linear molecules. For this reason we present a simple picture for understanding CDAD.

Consider Fig. 1(a) in which left and right circularly polarized light impinge on an oriented[43] diatomic molecule. The light propagates perpendicularly to the molecular axis and into the plane of the figure. Figure 1(a) represents the case of photoabsorption. Because the left and right cases are mirror images of each other (ignoring the hash-mark shading of the molecules), the two cases are physically identical, and no circular dichroism exists. However, if the photon has enough energy to ionize the molecule, and the electrons are collected in the plane at right angles to the light propagation direction (i.e., in the plane of the page), the left and right cases are no longer mirror images [Fig. 1(b)]—the photoelectron breaks the symmetry of the final state. For this reason, CDAD exists from oriented linear molecules.[26,46] In fact as shown in Ref. 26, CDAD in this case is not a small effect, as it already exists in the electric dipole approximation.[46]

If the linear molecules are not oriented,[43] but rather completely random in direction as in the gas phase, CDAD will not exist. However, after molecules absorb light, scatter off surfaces, etc., they can obtain an "alignment" in which all possible orientations of the molecular axis in space are not equally probable. CDAD can exist from these aligned molecules,[28] although the intensity of the CDAD signal will not be as strong as that from a perfectly oriented[43] molecule. Indeed, these CDAD signals have been measured.[31,32]

B. Experimental configuration for CDAD

The experimental configuration for the $(n + 1)$ CDAD experiment is given in Fig. 1 of Ref. 29. Light, linearly polarized along the laboratory frame z axis, induces n-photon absorption by the gas sample to yield a resonant intermediate state. Left or right circularly polarized light counterpropagating[47] with the first beam is then used to photoionize the sample. Photoelectrons are collected in the plane perpendicular to the propagation axis of the two beams. θ_k is defined as the angle between the direction of linear polarization and the electron collection direction.

C. CDAD theory

CDAD manifests itself in the difference between photoelectron signals obtained with left ($\mu_0 = +1$) and right ($\mu_0 = -1$) circularly polarized light.[26–32] As discussed in Ref. 28, due to the symmetry property[44]

$$\begin{pmatrix} 1 & 1 & L' \\ \mu_0 & -\mu_0 & 0 \end{pmatrix} = (-1)^{L'} \begin{pmatrix} 1 & 1 & L' \\ -\mu_0 & \mu_0 & 0 \end{pmatrix}, \quad (16)$$

only terms with $L' = 1$ switch sign upon changing from left to right polarization and thus only these terms contribute to CDAD. All the major features of CDAD follow from this fact. For a cylindrically symmetric system which displays alignment but not orientation, both L and $\mathbf{L}$ are even for symmetry reasons.[22,33] Because $L' = 1$, it follows from the triangle relationship[44] implied by the 3-j symbols involving L, L', and $\mathbf{L}$ in Eq. (15b) that $L = \mathbf{L}$ for CDAD. This fact was used without proof in Ref. 29 along with the Kronecker delta in Eq. (13) to derive the simple expression for the CDAD intensity $I_{\mathrm{CDAD}}(\theta_k)$:

$$I_{\mathrm{CDAD}}(\theta_k) = \sum_{\mathbf{L}} a_{\mathbf{L}} P^1_{\mathbf{L}}(\cos\theta_k), \quad (17a)$$

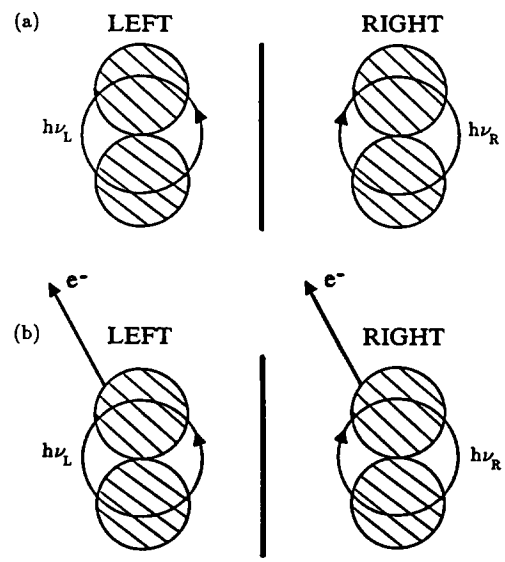

FIG. 1. A simple illustration of the physical basis for CDAD.

where

$$a_L = A_L \bar{\beta}_L \tag{17b}$$

and

$$\bar{\beta}_L = \frac{i}{\pi}\left[\frac{3(2L+1)}{2L(L+1)}\right]^{1/2} \beta_{L11}^{L1}, \tag{18}$$

$P_L^1(\cos\theta)$ is an associated Legendre polynomial. Equations (17) and (18) are obtained from Eqs. (14) and (15) by fixing the experimental configuration at $(\theta_p,\phi_p) = (90°,0°)$ and $\phi_k = 90°$. The fact that the indices L for the alignment and the photoelectron are the same is what makes CDAD such a useful probe of alignment.

The J dependence of $\bar{\beta}_L$ can be factored out[30,32]:

$$\bar{\beta}_L(J') = X_L(J')\tilde{\beta}_L, \tag{19}$$

where $\tilde{\beta}_L$ is explicitly independent of J'; it depends on J' only through the variation of the cross section with the photoelectron kinetic energy. Because rotational spacings are small, we can ignore this latter dependence and treat $\tilde{\beta}_L$ as a constant. The expression for $X_L(J')$ is

$$X_L(J') = (-1)^{J'+S'+\Lambda'}(2J'+1)(2N'+1) \times \begin{Bmatrix} J' & N' & S' \\ N' & J' & L \end{Bmatrix} \begin{pmatrix} N' & N' & L \\ \Lambda' & -\Lambda' & 0 \end{pmatrix}. \tag{20}$$

For photoionization of a $^2\Sigma$ state such as the $A\,^2\Sigma$ state of NO, $\Lambda' = 0$ and $S' = 1/2$. In this case, X_0 and X_2 become

$$X_0(J') = (2J'+1)^{1/2}, \tag{21}$$

$$X_2(J') = \frac{-1}{4}\left[\frac{(2J'+1)(2J'-1)(2J'+3)}{J'(J'+1)}\right]^{1/2}. \tag{22}$$

Note that Eqs. (21) and (22) are independent of N'.

IV. EXPERIMENT 2: PINDAD

A. Experimental configuration for PINDAD

The experimental configuration for PINDAD is identical to that for CDAD except that the circularly polarized ionizing probe beam is replaced by a linearly polarized beam in which the polarization vector *is always directed along the photoelectron collection direction.*

B. PINDAD theory

The PINDAD configuration requires $(\theta_p,\phi_p) = (\theta_k,\phi_k)$ in Eq. (14). Using the relations[48]

$$Y_{L0}(\theta_k,\phi_k) = (-1)^{L'-L}(2L+1)^{1/2}\sum_{M'} \times \begin{pmatrix} L & L' & L \\ -M' & M' & 0 \end{pmatrix} Y_{L-M'}(\theta_k,\phi_k)\, Y_{L'M'}(\theta_k,\phi_k) \tag{23}$$

and

$$Y_{L0}(\theta_k,\phi_k) = \left[\frac{(2L+1)}{4\pi}\right]^{1/2} P_L(\cos\theta_k), \tag{24}$$

it follows directly that

$$I_{\text{PINDAD}}(\theta_k) = \sum_L a'_L\, P_L(\cos\theta_k), \tag{25a}$$

where

$$a'_L = A_L \beta_L \tag{25b}$$

and

$$\beta_L = \frac{(4\pi)^{1/2}}{3} K \sum_{\substack{l\lambda\mu \\ l'\lambda'\mu' \\ LL'}} \bar{r}_{fi}^{(\mu)}\, \bar{r}_{fi}^{(\mu')*} e^{i(\eta_l - \eta_{l'})}(-i)^l (i)^{l'} \times (2N'+1)(2J'+1)[(2L+1)(2l+1)(2l'+1)(2L+1)(2L'+1)]^{1/2} \times (-1)^{S'+J'+\Lambda'+\lambda'+\mu} \begin{Bmatrix} J' & N' & S' \\ N' & J' & L \end{Bmatrix} \begin{pmatrix} N' & N' & L \\ \Lambda' & -\Lambda' & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & L' \\ \mu' & -\mu & \mu-\mu' \end{pmatrix} \times \begin{pmatrix} L & L' & L \\ \lambda'-\lambda & \mu-\mu' & 0 \end{pmatrix} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & L \\ \lambda & -\lambda' & \lambda'-\lambda \end{pmatrix} \begin{pmatrix} 1 & 1 & L' \\ 0 & 0 & 0 \end{pmatrix}. \tag{26}$$

$P_L(\cos\theta)$ is a Legendre polynomial [in contrast to $P_L^1(\cos\theta)$ in Eq. (17a)].[44] Once again, the indices for the alignment and the photoelectron are the same. Note that an $L = 0$ term contributes to the PINDAD signal while it does not to the CDAD signal.

Although the β_L for PINDAD are different from the $\bar{\beta}_L$ for CDAD, the J' dependence of the two is the same. Thus, the PINDAD β_L can be factored in an exactly analogous way to Eq. (19):

$$\beta_L(J') = X_L(J')\tilde{\beta}'_L, \tag{27}$$

where $X_L(J')$ is given in Eq. (20).

V. DETERMINATION OF PHOTOFRAGMENT ALIGNMENT

In Ref. 30, we stated that the alignment of an initial state could be determined by measurement of $(1+1)$ CDAD through two different excitation branches. Further we stated that this alignment could be determined *independently* of the photoionization dynamics. Consider an initial state which requires only $\tilde{A}_0$ and $\tilde{A}_2$ for a complete description of the alignment. Then using Eqs. (5), (17b), and (19),

$$a_2 = A_2 \cdot \bar{\beta}_2 = [\tilde{A}_0 C_{02} + \tilde{A}_2 C_{22}] \cdot X_2 \tilde{\beta}_2. \tag{28}$$

In the ratio $R = a_2^i / a_2^k$ for two different excitation branches i

and k, the $\tilde{\beta}_2$ values cancel, thus eliminating the photoionization dynamics from R. The ratio R is then simply a combination of 3-j, 6-j, and 9-j symbols which can be evaluated analytically. Using Eqs. (8) and (28) we can derive an expression for the initial state alignment[30]:

$$A_0^{(2)} = \frac{(M_0^i - M_0^k R)}{(M_2^i - M_2^k R)}. \tag{29}$$

Simplified expressions for the M values can be obtained from Eqs. (21) and (22) and Tables I and II. For one-photon absorption the M expressions are given in Table I of Ref. 30. For two-photon absorption, the M expressions are given here in Table III. The H values in Table III are the two-photon line intensities given by Halpern *et al.*[49] The line intensities appear when we explicitly consider the reduced matrix elements [as in Eq. (1)] which we previously set equal to unity. Note that because the M values only appear as ratios in Eq. (29), they can all be multiplied by a constant without changing value of $A_0^{(2)}$. For mixed branches, such as $Q_{11} + P_{21}$, the M values for the individual branches are simply added (ignoring coherence effects).[32]

We now make a very important point: the ratio $R = a_2^i/a_2^k$ for CDAD will be equal to the ratio $R' = a_2'^i/a_2'^k$ for PINDAD. This result follows directly from the fact that the β's for both methods can be factored in the same manner, as shown in Eqs. (19) and (27). The photoionization dynamics cancel in R' in the same way as in R. Thus, Eq. (29) and the same M values can be used to obtain the initial state alignment for CDAD or PINDAD.

VI. COMPARISON OF CDAD AND PINDAD

It remains to be explored experimentally whether CDAD or PINDAD provides a distinct advantage over the other for determining initial state alignment. The experimental configurations for the two methods are similar enough that the two techniques can be used together. Nevertheless, the following points are relevant:

(1) For a given initial state alignment, the % CDAD (relative to the intensity of the left or right spectrum) will be approximately the same as the % change in the intensity of PINDAD over the whole spectrum.[50]

(2) Spectra are typically measured over 360° and then averaged.[31,32] The CDAD spectrum does not have to be obtained using left *and* right polarization, but rather just one of them. Two of the opposite 90° quadrants will then correspond to the "left" spectrum and the other two to the "right." On the other hand, all four quadrants of the PINDAD spectrum will be equivalent.

(3) The CDAD spectrum is determined as the difference between two measurements[31,32]; as such, it contains twice the error of a single PINDAD measurement. On the other hand, certain systematic errors are eliminated in a difference spectrum.

(4) The intensity of the CDAD spectrum at $\theta_k = 0°$ and $\theta_k = 90°$ is zero.[28,31,32] There is no corresponding fact for the PINDAD spectrum.

VII. SOME FURTHER COMMENTS ABOUT PINDAD

Three alternative ways for extracting initial state alignment with PINDAD exist. All take advantage of the fact that a_0' is obtainable from Eq. (25a).

The first method requires that the ratio of a_0' values, rather than the ratio of a_2' values, for two different branches be determined. An expression for the initial state alignment can be derived in an analogous way to the derivation of Eq. (29). However, the a_0' values will be less sensitive to the initial state alignment than the a_2' values.[51]

The second method recognizes the fact that the coefficients extracted from a spectra using Eq. (25a) are usually normalized by a_0; that is, instead of obtaining a_0', a_2', and a_4', one obtains 1, b_2', and b_4' where $b_2' = a_2'/a_0'$ and $b_4' = a_4'/a_0'$. The expression for b_2' can be written

$$b_2' = \frac{a_2'}{a_0'} = \frac{A_2 X_2 \tilde{\beta}_2'}{A_0 X_0 \tilde{\beta}_0'}. \tag{30}$$

The ratio $\tilde{\beta}_2'/\tilde{\beta}_0'$ is a constant, but unknown. However, it can be obtained by performing an independent experiment on an unaligned initial state.[52] A graph of b_2' vs the theoretical value of $(A_2X_2)/(A_0X_0)$ for a number of J values (after being corrected for population differences due to the temperature of the sample) will yield the ratio $\tilde{\beta}_2'/\tilde{\beta}_0'$ from the slope. Once this ratio is known, it can be used to extract an unknown state alignment from the b_2' value of a *single* PINDAD spectrum.

TABLE III. M expressions for (2 + 1) CDAD through the $A\,^2\Sigma$ state of NO [Hund's case (b)]. H is described in the text.

Branch	M_0	M_2
O	$H\frac{2(2J''-5)}{(J''-1)}$	$H\frac{5(J''+1)(2J''-5)}{(J''-1)(2J''-1)}$
P	$-H\frac{(J''+5)(2J''-3)}{J''(J''-1)}$	$H\frac{5(J''^2-7)(2J''-3)}{J''(J''-1)(2J''-1)}$
Q	$-H\frac{(2J''+5)(2J''-3)}{J''(J''+1)}$	$H\frac{15[J''(J''+1)(2J''+5)(2J''-3)+21]}{J''(J''+1)(2J''-1)(2J''+3)}$
R	$-H\frac{(J''-4)(2J''+5)}{(J''+1)(J''+2)}$	$H\frac{5[(J''+1)^2-7](2J''+5)}{(J''+1)(J''+2)(2J''+3)}$
S	$H\frac{2(2J''+7)}{(J''+2)}$	$H\frac{5J''(2J''+7)}{(J''+2)(2J''+3)}$

In the third method, the ratio of b_2' values for two different branches is obtained. This ratio is also independent of the photoionization dynamics although it depends on the initial state alignment in a quadratic manner. While the expressions for $A_0^{(2)}$ are simple to derive from Eq. (30), they are complicated in appearance in this case.

All three of the above methods depend on an accurate determination of the value of a_0'. This value represents a constant contribution to the angular distributions $[P_0(\cos\theta) = 1]$ and is directly affected by any unwanted constant background in the spectra. For this reason the ratio of a_2' coefficients for two different excitation branches might yield more quantitative results.

VIII. CONCLUSIONS

Two independent angular-resolved $(n+1)$ REMPI techniques for obtaining the alignment of gas phase atoms and molecules have been presented. Both techniques provide initial state alignment, independently of the photoionization dynamics. Whether or not one technique provides a distinct advantage over the other in providing quantitative results remains to be established experimentally. Because the two techniques differ only in the polarization of the ionizing laser, they are similar enough to be used together.

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[1]R. Bersohn and S. H. Lin, Adv. Chem. Phys. **16**, 67 (1969).
[2](a) M. C. Lin and G. Ertl, Annu. Rev. Phys. Chem. **37**, 587 (1986), and references therein; (b) G. O. Sitz, A. C. Kummel, and R. N. Zare, J. Vac. Sci. Technol. A **5**, 513 (1987); J. Chem. Phys. **87**, 3247 (1987).
[3]R. E. Drullinger and R. N. Zare, J. Chem. Phys. **51**, 5532 (1969).
[4]R. N. Zare, Ber. Bunsenges. Phys. Chem. **86**, 422 (1982).
[5]W. J. Kessler and E. D. Poliakoff, J. Chem. Phys. **84**, 3647 (1986).
[6]M. T. MacPherson, J. P. Simons, and R. N. Zare, Mol. Phys. **38**, 2049 (1979).
[7]G. W. Loge and J. R. Wiesenfeld, Chem. Phys. Lett. **78**, 32 (1981); J. Chem. Phys. **75**, 2795 (1981).
[8]R. Vasudev, R. N. Zare, and R. N. Dixon, J. Chem. Phys. **80**, 4863 (1984).
[9]G. E. Hall, N. Sivakumar, and P. L. Houston, J. Chem. Phys. **84**, 2120 (1986).
[10]M. Dubs, U. Bruhlmann, and J. R. Huber, J. Chem. Phys. **84**, 3106 (1986).
[11]F. Lahmani, C. Lardeux, and D. Solgadi, Chem. Phys. Lett. **129**, 24 (1986).
[12]U. Bruhlmann, M. Dubs, and J. R. Huber, J. Chem. Phys. **86**, 1249 (1987).
[13]M. R. S. McCoustra, J. A. Dyet, and J. Pfab, Chem. Phys. Lett. **136**, 231 (1987).
[14]J. A. Guest and F. Webster, J. Chem. Phys. **86**, 5479 (1987).
[15]M. A. O'Halloran, H. Joswig, and R. N. Zare, J. Chem. Phys. **87**, 303 (1987).
[16]J. Reuss, Adv. Chem. Phys. **30**, 389 (1975).
[17]P. R. Brooks, Science **193**, 11 (1976).
[18]D. H. Parker, K. K. Chakrovorty, and R. B. Bernstein, Chem. Phys. Lett. **86**, 113 (1982), and references therein.
[19]U. Fano and J. H. Macek, Rev. Mod. Phys. **45**, 553 (1973).
[20]D. A. Case, G. M. McClelland, and D. R. Hershbach, Mol. Phys. **35**, 541 (1978).
[21]C. H. Greene and R. N. Zare, Annu. Rev. Phys. Chem. **33**, 119 (1982).
[22]C. H. Greene and R. N. Zare, J. Chem. Phys. **78**, 6741 (1983).
[23]A. C. Kummel, G. O. Sitz, and R. N. Zare, J. Chem. Phys. **85**, 6874 (1986).
[24]U. Hefter, G. Ziegler, A. Matthews, A. Fischer, and K. Bergmann, J. Chem. Phys. **85**, 286 (1986).
[25]See D. C. Jacobs and R. N. Zare, J. Chem. Phys. **85**, 5457 (1986); D. C. Jacobs, R. N. Madix, and R. N. Zare, *ibid.* **85**, 5469 (1986) for a method to extract alignment information from angle-integrated cross sections. See also Refs. 2(b) and 23.
[26]R. L. Dubs, S. N. Dixit, and V. McKoy, Phys. Rev. Lett. **54**, 1249 (1985).
[27]R. L. Dubs, S. N. Dixit, and V. McKoy, Phys. Rev. B **32**, 8389 (1985).
[28]R. L. Dubs, S. N. Dixit, and V. McKoy, J. Chem. Phys. **85**, 656 (1986).
[29]R. L. Dubs, S. N. Dixit, and V. McKoy, J. Chem. Phys. **85**, 6267 (1986).
[30]R. L. Dubs, S. N. Dixit, and V. McKoy, J. Chem. Phys. **86**, 5886 (1987).
[31]J. R. Appling, M. G. White, T. M. Orlando, and S. L. Anderson, J. Chem. Phys. **85**, 6803 (1986).
[32]J. R. Appling, M. G. White, R. L. Dubs, S. N. Dixit, and V. McKoy, J. Chem. Phys. (to be published).
[33]S. N. Dixit and V. McKoy, J. Chem. Phys. **82**, 3546 (1985).
[34]For the specific case of a two-photon Q transition ($J' = J''$) between two electronic states which both have Σ symmetry or both have Π symmetry, etc. Equation (7) must be generalized. See Ref. 10.
[35]J. C. Tully, R. S. Berry, and B. J. Dalton, Phys. Rev. **176**, 95 (1968).
[36]A. D. Buckingham, B. J. Orr, and J. M. Sichel, Philos. Trans. R. Soc. London Sect. A **268**, 147 (1970).
[37]Y. Itikawa, Chem. Phys. **28**, 461 (1978).
[38]J. C. Hansen and R. S. Berry, J. Chem. Phys. **80**, 4078 (1984).
[39]S. N. Dixit, R. L. Dubs, and V. McKoy, J. Chem. Phys. (to be published).
[40]We have in mind the specific case of photoionization of the $A\,^2\Sigma$ state of NO.
[41]S. N. Dixit, D. L. Lynch, V. McKoy, and W. M. Huo, Phys. Rev. A **32**, 1267 (1985).
[42]R. R. Lucchese, G. Raseev, and V. McKoy, Phys. Rev. A **25**, 2572 (1982).
[43]In this context, "oriented" means the molecular axis is fixed in space.
[44]A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, 1974).
[45]J. E. Brady and G. E. Humiston, *General Chemistry: Principles and Structure*, 2nd ed. (Wiley, New York, 1978).
[46]N. A. Cherepkov, Chem. Phys. Lett. **87**, 344 (1982).
[47]Although Fig. 1 of Ref. 29 shows the two beams copropagating, it is more convenient experimentally to counterpropagate the beams. See Refs. 31 and 32.
[48]M. Weissbluth, *Atoms and Molecules* (Academic, New York, 1978).
[49]J. B. Halpern, H. Zacharias, and R. Wallenstein, J. Mol. Spectrosc. **79**, 1 (1980).
[50]R. L. Dubs (unpublished results).
[51]This result follows from the fact that $|C_{22}/C_{02}| > |C_{20}/C_{00}|$ in general.
[52]This independent experiment can be performed on a gas phase sample of NO, but might not be possible for an unstable photofragment.